(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 March 2003 (13.03.2003)

PCT

(10) International Publication Number
WO 03/021656 A2

(51) International Patent Classification[7]: H01L 21/316

(21) International Application Number: PCT/EP02/09259

(22) International Filing Date: 19 August 2002 (19.08.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/944,918 31 August 2001 (31.08.2001) US

(71) Applicant (for all designated States except US): INFINEON TECHNOLOGIES AG [DE/DE]; St.-Martin-Str. 53, 81669 München (DE).

(72) Inventor; and
(75) Inventor/Applicant (for US only): BRUCHHAUS, Rainer [DE/JP]; 2-12-35 Ushikubo-Higashi, Tsuzuki-ku, Yokohama-shi, Kanagawa 224-0014 (JP).

(74) Agent: EPPING, HERMANN & FISCHER; Ridlerstrasse 55, 80339 München (DE).

(81) Designated States (national): CN, JP, KR, US.

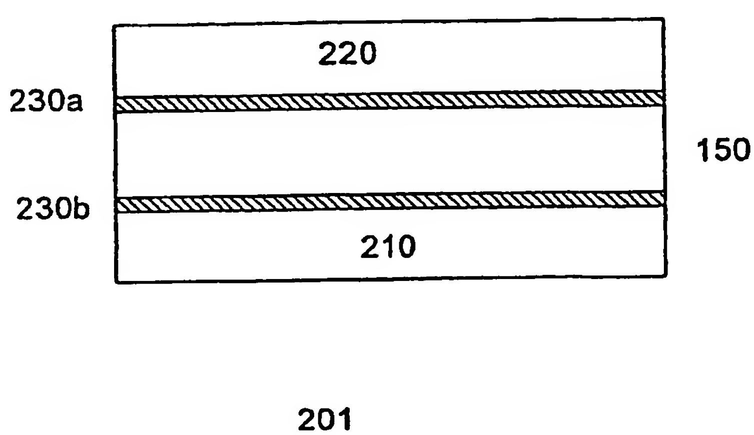
(84) Designated States (regional): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

BEST AVAILABLE COPY

(54) Title: IMPROVED MATERIAL FOR USE WITH FERROELECTRICS



(57) Abstract: A liner layer comprising TiO_2 enriched SRO is disclosed. The TiO_2 enriched SRO liner improves the reliability of ferroelectric materials such as PZT without adversely impacting or degrading the ferroelectric properties of the PZT. The SRTO, in one embodiment is sputtered using an SRO target doped with 1-10% TiO_2.

WO 03/021656 A2

IMPROVED MATERIAL FOR USE WITH FERROELECTRICS

FIELD OF THE INVENTION

The present invention relates to ferroelectric integrated circuits and, more particularly, to materials that reduces fatigue in the ferroelectric material.

BACKGROUND OF THE INVENTION

Ferroelectric metal oxide ceramic materials such as lead zirconate titanate (PZT) have been investigated for use in ferrolectric semiconductor memory devices. A memory cell of the ferroelectric memory device includes a capacitor which serves as the storage element. Fig. 1 shows a conventional ferroelectric capacitor 101. As shown, the capacitor comprises a ferroelectric metal oxide ceramic layer 150 sandwiched between first and second electrodes 110 and 120. The electrodes typically are formed from a noble metal such as platinum.

The ferroelectric capacitor uses the hysteresis polarization characteristic of the ferroelectric material for storing information. The logic value stored in the memory cell depends on the polarization of the ferroelectric capacitor. To change the polarization of the capacitor, a voltage which is greater than the

BNSDOCID: <WO_____03021656A2_I_>

switching voltage (coercive voltage) needs to be applied across its electrodes. The polarization of the capacitor depends on the polarity of the voltage applied.

An advantage of the ferroelectric capacitor is that it retains its polarization state after power is removed, resulting in a non-volatile memory cell. However, fatigue in the ferroelectric material occurs after a certain number of switching cycles. To reduce fatigue in the ferroelectric capacitor, strontium-ruthenium-oxide ($SrRuO_3$ or SRO) as a liner material directly attached between the ferroelectric film and the electrode has been proposed. SRO is typically formed by sputtering.

A problem, however, exists with the use of SRO as a liner material due to the instability of its forming compounds RuO_2 and SrO. Specifically RuO_2 is a volatile oxide and SrO easily forms $SrCO_3$ if it is exposed to the atmosphere. Some RuO_2 evaporates during the crystallization anneal of the amorphous film formed during sputtering, resulting in excess SrO in the SRO layer. This is undesirable because excess SrO produces flowerlike features on the surface of the SRO layer. Furthermore, SrO itself is an isolating material leading

to a performance degradation of the ferroelectric capacitor.

To counterbalance the loss of RuO_2 during crystallization, an SRO target with excess RuO_2 is used. However, the excess RuO_2 diffuses and reacts with the ferroelectric layer during high temperature crystallization of the ferroelectric material which degrades its ferroelectric properties.

From the foregoing discussion, it is desirable to provide an improved material which reduces fatigue without adversely impacting its ferroelectric properties.

SUMMARY OF THE INVENTION

The invention relates to the use of materials which reduces fatigue in ferroelectric materials without adversely affecting its ferroelectric properties. In one embodiment of the invention, the material comprises SRO which is enriched with TiO_2. The SRO comprises about 1-10 atomic weight percent (unless otherwise specified, all percentages are in atomic weight percent) of TiO_2. In one embodiment, the TiO_2 enriched SRO is formed on a substrate which is processed to include a first or bottom capacitor electrode. A ferroelectric material

such as PZT is formed on the TiO_2 enriched SRO. Subsequently, a second TiO_2 enriched SRO layer is formed on the ferroelectric layer followed by formation of the upper electrode. In one embodiment, the SRO enriched layer is formed by sputtering using an SRO target doped with 1-10 percent % TiO_2.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 shows a conventional ferroelectric capacitor;

Fig. 2 shows a ferroelectric capacitor in accordance with one embodiment of the invention;

Fig. 3 shows an illustrative system for depositing the TiO_2 enriched SRO layer in accordance with one embodiment of the invention; and

Fig. 4 shows an SRTO layer after a crystallization anneal.

DETAILED DESCRIPTION OF THE INVENTION

Fig. 2 shows a ferroelectric capacitor 201 in accordance with one embodiment of the invention. Such a capacitor, for example, is used to form a ferroelectric memory cell of a ferroelectric memory IC. As shown, the capacitor comprises first and second electrodes 210 and

220. The electrodes are formed from, for example, platinum or a noble metal such as Ir, Pd, IrO_2 or other conducting oxides. A ferroelectric layer 150 is located between the electrodes. In one embodiment, the ferroelectric material comprises PZT or lead-lanthanum-zirconium-titanate (PLZT). Other types of ferroelectric material, such as Strontium-bismuth-tantalate (SBT) may also be used.

Liner layers 230a-b are provided between the electrodes and the ferroelectric layer to reduce fatigue in the ferroelectric layer. In accordance with the invention, the liner layer comprises TiO_2 enriched SRO (e.g., TiO_2 doped SRO). The TiO_2 increases the stability of the SRO layer which in turn, reduces the formation of flowerlike features. In one embodiment, the SRO is doped with 1-10 percent of TiO_2. Greater than 10% of TiO_2 in the SRO film can increase the sheet resistance of the TiO_2 enriched SRO layer beyond desirable limits, thus adversely impacting the performance of the capacitor. In one embodiment, the thickness of the TiO_2 enhanced SRO layer is about 5-50nm, the ferroelectric layer is about 100-200nm, and the electrode is about 10-100nm. The preferred thickness of the TiO_2 doped SRO is in the range

of 5-50 nm, typical PZT thicknesses are 100-200 nm, Pt 10-100 nm.

The TiO_2 enriched SRO layer is sputtered, in one embodiment, on the substrate. Fig. 3 shows a sputtering system 301 used to deposit the TiO_2 enriched SRO layer. The system includes a substrate support 305 on which a substrate is mounted. The substrate has been processed to include, for example, a conductive layer such as platinum to serve as the bottom electrode of the capacitor. Depending on the process, the conductive layer can be patterned or not. The system also includes a sputtering target 310 comprising a SRO ceramic compound enriched with 1-10 percent of TiO_2.

During the sputtering process, atoms from the target react to form an amorphous layer 330 consisting of SrO, TiO_2 and RuO_2 on the substrate. The parameters of the sputtering process, for example, are as follows:

Pressure: 0.5 -1 Pa

Temperature: room temperature to 650°C

Power: 500-1000 W

Reactive gas: Ar gas with 5 - 50 % volume weight %

After deposition, the amorphous film is crystallized by an annealing process at, for example, a temperature of 450 - 700°C for about 30 seconds to 5 minutes. During

the anneal, excess SrO is transformed into $SrTiO_3$ (STO). STO is a stable material having a perovskite structure similar to that of PZT and other types of ferroelectric materials. The TiO_2 enriched SRO layer may also contain unreacted TiO_2 grains 434, as shown in Fig. 4. The STO and unreacted TiO_2 grains serve as nucleation sites for the subsequently formed ferroelectric layer, triggering a very uniform grain structure in the ferroelectric layer and improved ferroelectric properties.

After the crystallization of the TiO_2 enriched SRO layer, the process continues to form the ferroelectric capacitor and completion of the IC. This, for example, includes forming the ferroelectric layer, the second TiO_2 enriched SRO layer, upper electrode, interconnects and interlevel dielectrics, passivation layer and packaging.

While the invention has been particularly shown and described with reference to various embodiments, it will be recognized by those skilled in the art that modifications and changes may be made to the present invention without departing from the spirit and scope thereof. The scope of the invention should therefore be determined not with reference to the above description but with reference to the appended claims along with their full scope of equivalents.

BNSDOCID: <WO_______03021656A2_I_>

What is claimed is:

1. A method for forming a ferroelectric capacitor comprising:

providing a substrate having a first conductive layer formed thereon, the first conductive layer serves as a electrode of the capacitor;

depositing a first amorphous liner layer on the electrode;

depositing a ferroelectric layer on the first liner layer;

depositing a second amorphous liner layer on the ferroelectric layer; and

depositing a second conductive layer on the liner layer, the second conductive layer serves as a second electrode, wherein the liner layer comprises SRO enriched about 1-10% TiO_2 weight percent, wherein the liner layers improve the properties of the ferroelectric layer.

2. The method of claim 1 wherein the ferroelectric layer comprises PZT.

3. The method of claim 2 wherein the first electrode comprises a noble metal.

4. The method of claim 3 wherein the first electrode comprises platinum.

5. The method of claim 1 wherein the electrodes comprise a noble metal.

6. The method of claim 5 wherein the electrodes comprise platinum.

7. The method of claim 1,2,3,4,5 or 6 further comprises an annealing process to crystallize the TiO_2 enriched SRO layer.

8. The method of claim 7 wherein the annealing process comprise heating the TiO_2 enriched SRO layer at a temperature of about 650°C for about 30 sec.

9. The method of claim 8 further comprising the steps for completing a ferroelectric memory IC.

10. The method of claim 7 further comprising the steps for completing a ferroelectric memory IC.

11. A method for forming a ferroelectric capacitor comprising:

depositing a first amorphous layer on a substrate;

depositing a ferroelectric layer on the first liner layer;

depositing a second amorphous liner layer on the ferroelectric layer; and

depositing a second conductive layer on the liner layer, the second conductive layer serves as a second electrode, wherein the liner layer comprises SRO enriched with about 1-10% TiO_2, wherein the liner layers improves the properties of the ferroelectric layer.

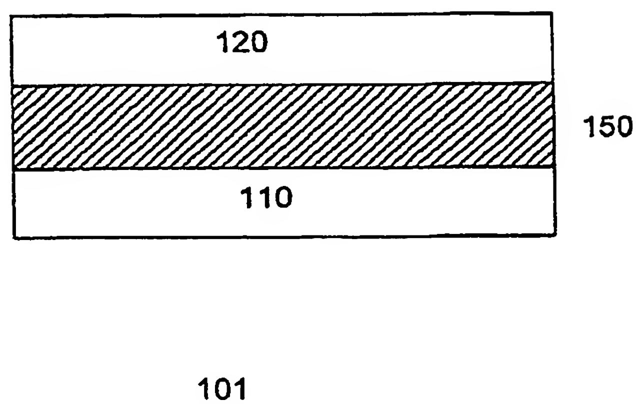


Fig. 1

PRIOR ART

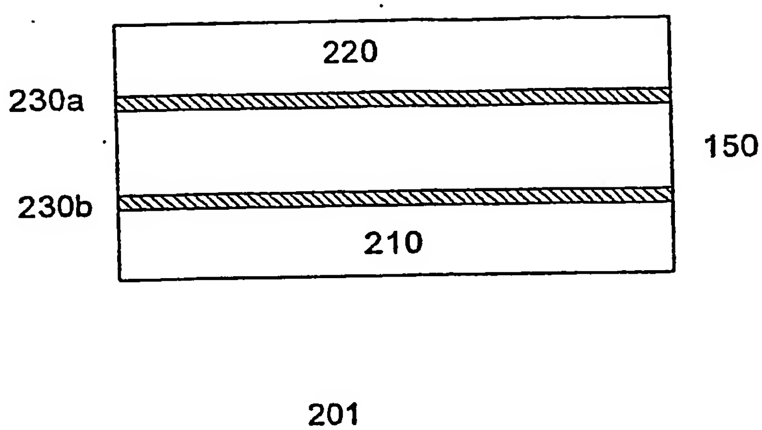


Fig. 2

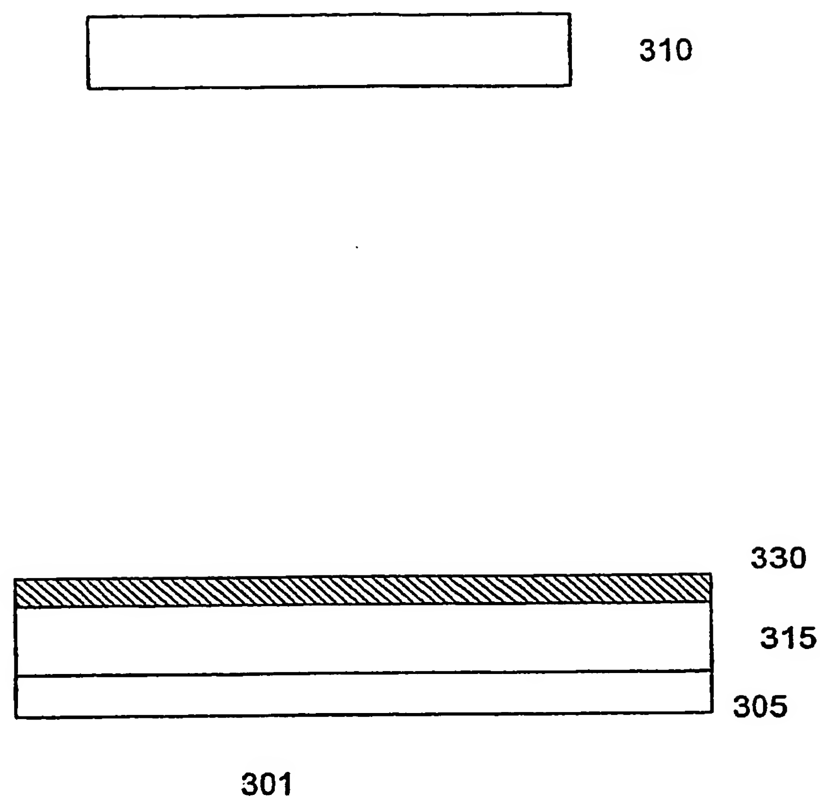


Fig. 3

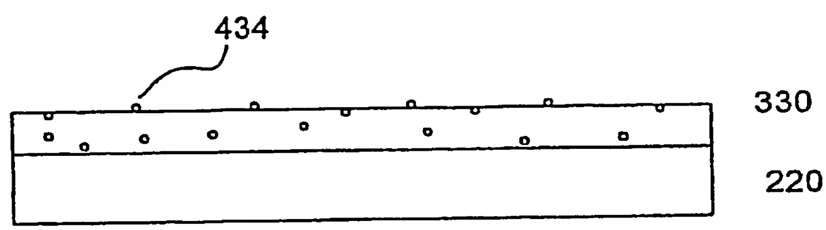


Fig. 4

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 March 2003 (13.03.2003)

PCT

(10) International Publication Number
WO 03/021656 A3

(51) International Patent Classification[7]: H01L 21/316, 21/02

(21) International Application Number: PCT/EP02/09259

(22) International Filing Date: 19 August 2002 (19.08.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/944,918 31 August 2001 (31.08.2001) US

(71) Applicant *(for all designated States except US)*: INFINEON TECHNOLOGIES AG [DE/DE]; St.-Martin-Str. 53, 81669 München (DE).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: BRUCHHAUS, Rainer [DE/JP]; 2-12-35 Ushikubo-Higashi, Tsuzuki-ku, Yokohama-shi, Kanagawa 224-0014 (JP).

(74) Agent: EPPING HERMANN FISCHER PATENTANWALTSGESELLSCHAFT MBH; Ridlerstrasse 55, 80339 München (DE).

(81) Designated States *(national)*: CN, JP, KR, US.

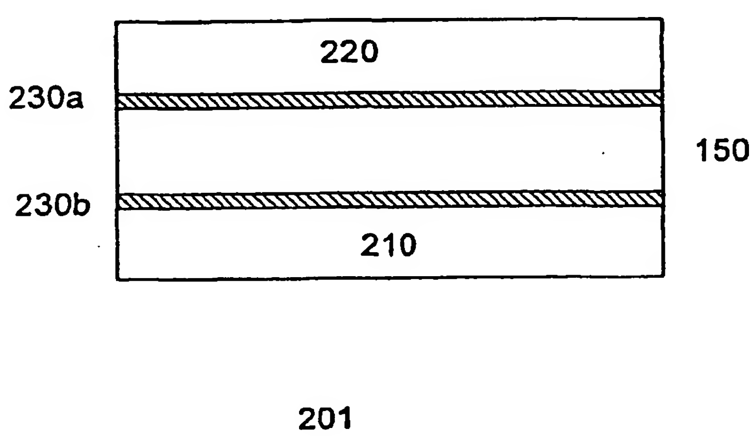
(84) Designated States *(regional)*: European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR).

Published:
— *with international search report*

(88) Date of publication of the international search report: 20 November 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: IMPROVED MATERIAL FOR USE WITH FERROELECTRICS



(57) Abstract: A liner layer comprising TiO_2 enriched SRO is disclosed. The TiO_2 enriched SRO liner improves the reliability of ferroelectric materials such as PZT without adversely impacting or degrading the ferroelectric properties of the PZT. The SRTO, in one embodiment is sputtered using an SRO target doped with 1-10% TiO_2.

WO 03/021656 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/09259

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L21/316 H01L21/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 194 228 B1 (CROSS JEFFREY S ET AL) 27 February 2001 (2001-02-27) column 3, line 60 -column 5, line 27; figure 1	1-11
Y	US 6 218 233 B1 (TAKEMURA KOICHI) 17 April 2001 (2001-04-17) column 11, line 38 - line 49 column 11, line 15 -column 12, line 8	1-11
A	US 6 096 434 A (NOGUCHI TAKAO ET AL) 1 August 2000 (2000-08-01) column 13, line 24 - line 38	1,11
A	US 2001/007364 A1 (CROSS JEFFREY SCOTT ET AL) 12 July 2001 (2001-07-12) paragraph '0034! - paragraph '0045!; figure 1A	1,11

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 March 2003	12/03/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Götz, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/09259

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 128 178 A (NEWNS DENNIS MERTON) 3 October 2000 (2000-10-03) column 5, line 2 - line 3; figure 3	1,11

BNSDOCID: <WO_______03021656A3_I_>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 02/09259

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6194228 B1	27-02-2001	JP 11195768 A	21-07-1999
US 6218233 B1	17-04-2001	JP 3169866 B2	28-05-2001
		JP 11145391 A	28-05-1999
		TW 425691 B	11-03-2001
		US 2001000923 A1	10-05-2001
US 6096434 A	01-08-2000	JP 11026296 A	29-01-1999
US 2001007364 A1	12-07-2001	JP 2001196547 A	19-07-2001
		DE 10100695 A1	26-07-2001
		TW 473991 B	21-01-2002
US 6128178 A	03-10-2000	JP 2000058792 A	25-02-2000
		KR 2000011294 A	25-02-2000

BNSDOCID: <WO_______03021656A3_I_>

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☑ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ______________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.